

Fabrication and Characterization of pH-Responsive, Nanoparticle-Attached Porphyrins for Singlet Oxygen Production

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ABSTRACT

The goal of this work was to understand if singlet oxygen ($^1\text{O}_2$) production from an immobilized dye could be regulated directly on support media such as titania and silica nanoparticles. Two types of pH-responsive, nanoparticle-attached sensitizers were prepared and tested for $^1\text{O}_2$ production as a function of pH. The colloiddally dispersed titania-attached 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin (titania-TCPP) behaved as a single-phase colloidal sensitizer at pH 1.0-3.3 with quantum yields of $^1\text{O}_2$ production (Φ_Δ) between 0.20 and 0.25, as a heterogeneous particle sensitizer at pH 3.5-6.0 with Φ_Δ between 0.25 and 0.50, and as homogeneous free TCPP molecules in alkaline solutions with $\Phi_\Delta = 0.53$. Φ_Δ for colloidal silica nanoparticle-attached meso-tetra(N-methyl-4-pyridyl)porphine (silica-TMPyP) was pH-dependent as well, showing the higher Φ_Δ in weak acidic solution. The changes in Φ_Δ were fully consistent with pH dependent adsorption of porphyrins on nanoparticle surface. Those studies provide insights into the effect of support media on the photosensitization ability of porphyrin molecules, and the possibility of manipulation between photosensitization and recovery based on different type of support media.

Keywords: singlet oxygen, silica, titania, pH-responsive sensitizer

INTRODUCTION

The use of heterogeneous sensitizers for singlet oxygen ($^1\text{O}_2$) photooxidation in a solution facilitates product separation and analysis. The first heterogeneous sensitizer was a polymer-attached rose Bengal,^{1,2} which was followed by a series of immobilized dyes on polymers, organic and inorganic oxides.³⁻⁹ Despite of the enormous advantages in terms of separation and purification, challenges pertinent to the use of immobilized sensitizers still exist: dye recovery is usually achieved at the expense of photosensitization ability.^{2,4} Our recent work showed that the strong adsorption of porphyrin molecules on titania surface at low pH favored electron transfer reaction and hence resulted in an inefficient $^1\text{O}_2$ production.¹⁰ However, it has not been fully understood how the interaction of a dye with its support media would affect photosensitization.

RESULTS AND DISCUSSION

The goal of this work was to understand if $^1\text{O}_2$ production from an immobilized dye could be regulated directly on support media such as titania and silica. Two types of pH-responsive, nanoparticle-attached sensitizers were prepared and tested for $^1\text{O}_2$ production as a function of pH by photochemical techniques such as time-resolved laser and steady-state photolysis. Our results show that the colloiddally dispersed Titania-attached 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin (titania-TCPP) behaved as a single-phase colloidal sensitizer at pH 1.0-3.3 with quantum yields of $^1\text{O}_2$ production (Φ_Δ) between 0.20 and 0.25, as a heterogeneous particle sensitizer at pH 3.5-6.0 with Φ_Δ between 0.25 and 0.50, and as homogeneous free TCPP molecules in alkaline solutions with $\Phi_\Delta = 0.53$.¹⁰ Φ_Δ for colloidal silica nanoparticle-attached meso-tetra(N-methyl-4-pyridyl)porphine (silica-TMPyP) was pH-dependent as well, showing higher Φ_Δ in weak acidic solution. The changes in Φ_Δ were fully consistent with pH dependent adsorption of porphyrins on nanoparticle surface.

The recovery of porphyrins was achieved when porphyrin molecules were strongly adsorbed onto nanoparticle surface. For instance, free TMPyP is soluble in a wide pH range of 2-10 in water. Based on the pH-responsive stability of colloidal silica-TMPyP nanoparticles, the recovery of TMPyP was accomplished through the formation of silica-TMPyP aggregates in weak alkaline solutions by centrifugation. To test this, silica-TMPyP was precipitated by centrifugation at different pH. The supernatant was analyzed by absorption spectroscopy to quantify the remaining TMPyP concentrations at 422 nm using $\epsilon = 2.3 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$. The recovery yields of TMPyP were dramatically increased up to over than 90% when pH was above neutral where the electrostatic attraction favored the association of positively charged pyridinium groups in TMPyP and the negatively charged silica nanoparticles. However, at lower pH where the surface charge of silica was positive, the adsorption of cationic TMPyP onto the silica surface was inhibited. Thus, TMPyP was therefore dissolved into water and could not be removed with silica particles from the solutions. Figure 2 shows the effects of pH on recovery yields of TMPyP, in which the best sensitizer recovery yield of 92% for silica-TMPyP at pH 8-10 and a dramatic decrease to 10% at pH 2, were obtained. Similarly, the recovery yields of 99.8% for TCPP and 98.8% for titania were obtained in acidic conditions for titania-TCPP sensitizer.¹⁰

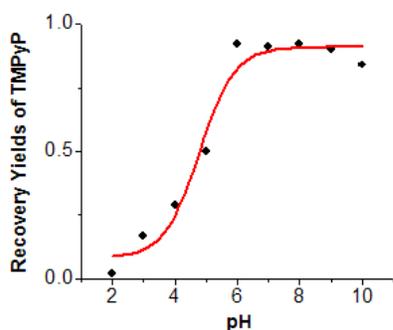


Figure 1. Effects of pH on recovery yields of 5.0×10^{-5} M TMPyP adsorbed onto 2.0 g/L silica nanoparticles.

CONCLUSION

Those studies provide insights into the effect of support media on the photosensitization ability of porphyrin molecules, and the possibility of manipulation between photosensitization and recovery based on different type of support media. The use of immobilized sensitizers generates no secondary pollution products and minimizes environmental and public health impacts associated with the use of chemicals. Control of $^1\text{O}_2$ production at different pH has significance in development of selective sensitizers for various applications such as practical use in photodynamic therapy. Moreover, photo-initiated excitation and deactivation via energy- or electron-transfer processes are a broad fundamental class of transformations. The Incorporation of organic molecules into nanoparticles has been extensively investigated to construct functional hybrid materials. As a consequence, the development of novel devices that controls photochemical pathways has far reaching impact beyond the applications described in this proposal. The success of the project will provide a better understanding of nanoparticle-dye based surface chemistry, and has significance in many areas as long as immobilized dye devices are concerned.

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